Electrochemical Reactors for Wastewater Treatment

Thorben Muddemann[1],*,‡, Dennis Haupt[2],*,‡, Michael Sievers[2], Ulrich Kunz[1]

Abstract

Regarding the treatment of (waste)water, electrochemical processes have various advantages over other methods. They are robust, easy to operate and flexible in case of fluctuating wastewater streams. In addition, a relatively broad spectrum of organic and inorganic impurities can be removed. This contribution provides an overview of electrochemical reactors for water, process water, and wastewater treatment, which are already in technical-scale operation or subject of research. Some essential basics of electrochemical processes for the treatment of water are presented and examples for applications are given. This is followed by a description of the reactors.

Keywords: Electrochemical reactors, Electrolysis, Microbial fuel cell, Water purification

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1 Introduction

Electrochemical reactors are apparatuses for material transformations forced by electric current. Oxidation occurs at the anode and reduction at the cathode. The basic principles and designs of such reactors have been described in detail several times in literature [1–3]. This contribution focuses on an overview of electrochemical reactors for the treatment of water, process water, and wastewater. First, basic principles of electrochemical processes for the treatment of water are presented and examples for applications are given. This is followed by a description of the reactors. Technical operating data and design details such as current densities, voltages, and electrode spacings are not given in this overview article as this would exceed its scope. Reactor designs are very specific regarding their application due to the various (waste)water compositions and the intended cleaning objective. For further information, please refer to the relevant literature.

The requirements for process water and wastewater treatment with electrochemical processes depend on the quantity and composition of the water to be treated and of the target substances for elimination. The designs and modes of operation of electrochemical reactors are therefore diverse. The dimensions range from built-in appliances in domestic water pipes with dimensions of several cm to industrial plant complexes with areas of several 100 m^2.

The treatment of complex (waste)water for an economic application usually consists of a combination of different physical, biological, and chemical processes. These processes include sedimentation, filtration, flotation, precipitation/flocculation, aerobic and anaerobic processes, membrane processes, photocatalysis, adsorption, stripping, extraction, distillation, UV disinfection and ozonation.

In this context, electrochemical processes have also contributed - in some cases for decades [4, 5]. These are also often combined with other processes such as aerobic and anaerobic processes [6, 7], membrane processes [8, 9], photocatalysis [10], adsorption [11] and ozonation [12, 13].

A distinction is made between processes in which current is supplied from outside (electrolysis) and processes in which electrical current is generated from substances contained in the water (galvanic element). So far, processes implemented in practice on a technical scale are solely electrolysis processes. The tasks of technically applied electrochemical reactors are:

- precipitation of dissolved ions for downstream solid/liquid separation (electrocoagulation) [14],
- production of microbubbles for the separation of solids by flotation (electroflotation) [15],
- separation and concentration of dissolved ions and molecules (electrodialysis) under the influence of an applied potential difference [16],

[1] Thorben Muddemann (corresponding author), Prof. Ulrich Kunz
Clausthal University of Technology, Institute of Chemical and Electrochemical Process Engineering, Leibnizstrasse 17, 38678 Clausthal-Zellerfeld, Germany.
E-Mail: thorben.muddemann@tu-clausthal.de

[2] Dennis Haupt (corresponding author), Prof. Michael Sievers
Clausthal University of Technology, CUTEC Clausthal Research Center for Environmental Technologies, Leibnizstrasse 23, 38678 Clausthal, Germany.
E-Mail: dennis.haupt@cutec.de

‡These authors contributed equally to this work.

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– extraction or separation of metals from aqueous wastewater streams by electrolysis (electrolytic metal separation) [17],
– emulsion splitting of surfactant-containing (washing) waters [2, 18],
– in situ generation of active chlorine species for disinfection (hypochlorite electrolysis) [19].

The advantages of electrochemical processes are robustness, simple operational management and short-term adaptation to wastewater fluctuations by simply switching the power on and off and/or adjusting the current density.

In addition, they are able to eliminate a relatively wide range of organic and inorganic contaminants. Necessary chemicals are formed in situ and only few (e.g., for a Fenton process) or no additional chemicals are required for operation. In particular, the combination of electricity from renewable sources with the in situ production of chemicals (= relinquishment/reduction of additional chemicals) enables sustainable solutions for the future.

Electrochemical treatment plants for treatment of brackish water, drinking water, or process water have volumetric flow rates from a few liters per day up to 20 000 m^3d^{-1} [20, 21]. In wastewater practice these are frequently used for small to medium wastewater volumetric flow rates up to approx. 500 m^3d^{-1}, e.g., oil production, washing water for cars, process water for the textile and chemical industry. This is due to the higher concentrations of the constituents in low volumetric wastewater flow rates as well as the increase in electricity consumption proportional to the volume of wastewater. Furthermore, the electrode costs impede the treatment of higher volumetric wastewater flow rates.

Price-intensive electrodes with electrochemical catalysts and specific coatings make a particular contribution to this. In processes with typical electrode consumption (dissolution), such as electrocoagulation, the electrode costs are part of the operating costs.

In addition to the state of the art electrolysis processes mentioned above, other more recent processes with high application potential are of interest. They can also have a degrading character on organic load and ideally contain the potential for complete, residue-free mineralization as a solution against increasing water scarcity. In the future, these processes in particular will have increased application potential for substances that are difficult or impossible to biodegrade. Those processes are currently used for a small number of industrial waters and are aiming for a wider application or are still under development:

– generation of radicals for the oxidation/reduction of organic impurities (electrochemical oxidation/reduction),
– in situ hydrogen peroxide production as an oxidizer for ozone (peroxone) and/or UV treatment processes (H_2O_2 electrolysis),
– in situ H_2O_2 activation for radical generation (electro-Fenton, photo-electrolysis),
– in situ ozone generation for use as oxidizing agent (electrolysis based on boron-doped diamond electrodes),
– precipitation by taking advantage of the pH value shift at the electrodes (electrostatic precipitation).

These purely electrochemical processes are combined with other processes. For example, the combination of electrochemistry and microbiology enables further novel applications such as the bio-electrochemical oxidation of dissolved organic wastewater constituents with simultaneous power generation (microbial fuel cell).

The new processes as well as the electrodialysis have the potential to treat both higher concentrated smaller and low concentrated larger quantities of water economically. Furthermore, they can also make a valuable contribution to the complete elimination or degradation of water impurities or micropollutants such as X-ray contrast agents that are difficult to biodegrade. However, in this context it is important to control or avoid the formation of unwanted by-products for each application.

Tab. 1 gives an overview of existing and possible applications. It becomes clear that electrochemical processes are predominantly used in the field of industrial wastewater treatment, whereby electrodialysis finds wider application. A trend-setting approach in the industrial sector is the production-integrated water/wastewater treatment with separation and recovery of ingredients as valuable substances. Simultaneously, the reduction of water consumption by closing the water cycle is possible [22]. Selective separation techniques are just as necessary as non-specific oxidation processes, since the latter include the possibility of decomposing organic (micro)-pollutants without residues to achieve good water qualities. Electrochemical processes can be used in both applications. Recently, they have received increased attention, as the increasing number of publications and contributions at international conferences demonstrate. There are some overview papers on electrochemical water/wastewater treatment [23–26], but only a few on reactors and their designs [1–3]. Due to the wide range of possible applications and the numerous processes in the water and wastewater sector, electrodes, materials, reactor designs and interconnections vary to a wide extend.

2 Functionality of Electrochemical Reactors

Electrochemical reactions are carried out in special reactors. The basic principles of these systems have been described in detail [47]. The following is a summary of the processes within an electrochemical reactor.

An electrochemical system consists of at least two electrodes – an anode and a cathode – and an intermediate space filled with electrolyte. For electrochemical characterizations, the system can additionally be extended by reference electrodes, whereby these do not participate in the target reactions.

The electrical circuit is closed via electrical wires either with a voltage source (electrolysis cell) or an electrical load (galvanic element). In many applications, a separator (membrane or diaphragm) separates the reactor into an anode and cathode compartment. The electrolyte surrounding the anode is named anolyte and the electrolyte on the cathode side is called catholyte. Fig. 1a shows the general set-up of an electrolysis cell, while the function of a galvanic element is shown in Fig. 1b.

Oxidation reactions take place at the anode

$$Red \rightarrow Ox + z\ e^- \quad (1)$$

and reduction reactions at the cathode

$$Ox + z\ e^- \rightarrow Red \quad (2)$$

Table 1. Overview of electrochemical water treatment processes: tasks and field of application; in brackets: possible applications aspiring to practice, development status different.

Substance	S	C	DM	DI	DO	GB	Task	Application examples*	Ref.
Concentrating Applications									
Electrocoagulation	X	X	(X)		X		Release of metal ions (Fe^{2+}, Al^{3+}) for agglomeration	Metal industry, Textile industry, Car wash industry	[2, 27, 28]
Electroflotation	X		(X)		(X)		Bubble generation for flotation of particles	Metal industry, Textile industry, Car wash industry	[2, 29, 30]
Electrodialysis			X	X	X	(X)	Electric field generation for membrane-based ion separation	Brackish water desalination, Water softening	[2]
Electrolytic Metal Deposition			X				Metal ion discharge for particle formation and electrode deposition	Electroplating, metal industry	[2, 14, 31]
Electrochemical Precipitation			X	X			Precipitation of salts by pH gradients near electrodes	(Water softening, phosphate precipitation)	[2, 32]
Degrading Applications									
Emulsion Splitting Electrolysis		X			X		Neutralization and destabilization of micelles	Wash water treatment for motor vehicles (road/rail)	[2, 18]
Electrochemical Oxidation	(X)	X	(X)		X	X	Generation of oxidative/reductive/radical species	Municipal wastewater (toilet wastewater), Chemical industry, Groundwater, Ballast water, Landfill leachate etc.	[2, 33–39, 77, 83]
Electro-Fenton	(X)	X	(X)		X	X	Production of radical species with auxiliary iron	(Textile industry, paper industry)	[2, 40, 41]
Microbial Fuel Cell	(X)	X			X	(X)	Microbiological metabolism of organic compounds	(Food/beverage industry, domestic waste water)	[2]
Chemical Producing Applications									
Hypochlorite Electrolysis						X	Production of chlorine-based disinfectants	Raw water disinfection, drinking water disinfection, textile industry, swimming pool disinfection	[31, 42, 43]
Hydrogen Peroxide Electrolysis					(X)	X	Production of the oxidizing agent hydrogen peroxide	Partial disinfection of circulation water	[44]
Ozone Electrolysis					X	X	Generation of the oxidizing agent ozone	Micropollutant degradation, disinfection	[31, 45, 46]

S: suspend; C: colloides; DM: dissolved metals; DI: dissolved ions; DO: dissolved organics; GB: germs, bacteria.

with z as the number of exchanged electrons, *Ox* and *Red* are any dissolved, oxidized and reduced species, respectively.

If the reactions and the associated electrochemical standard potentials (see "galvanic series") are known, the potential

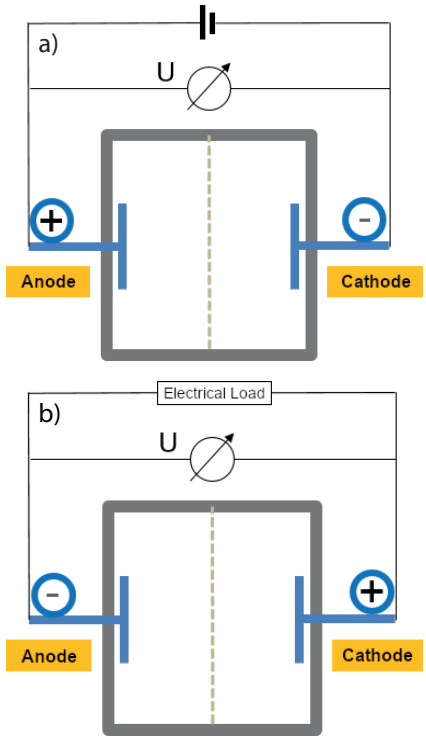

Figure 1. Schematic illustration of the (a) electrolysis process and (b) the galvanic element.

difference (E_Z) of the two half-cell reactions results in the thermodynamic equilibrium voltage.

$$E_Z = E_{Red} - E_{Ox} \tag{3}$$

From the potential difference as well as the free enthalpy of reaction it can be concluded to what extent the reactions of the cell take place spontaneous.

- $E_Z < 0$: non-spontaneous reaction – electrolysis system
- $E_Z > 0$: spontaneous reaction – galvanic element

Thus, chemical reactions at the anode and cathode are forced in the electrolysis cell by the influence of the applied electric current, while these occur spontaneously in galvanic elements (fuel cell, battery).

As only electrolysis and fuel cell technology are used in electrochemical wastewater technology, this will be focused in the following.

In detail, electrochemical reactions take place in several sub-steps at the electrodes (Fig. 2). If the sub-steps of the reaction do not limit the reaction rate, the current I determines the reaction rate n/t (mol/time) of the desired reaction according to Faraday's law, with the current I and the Faraday constant F:

$$\frac{n}{t} = \frac{I}{z\,F} \tag{4}$$

Otherwise, each of the sub steps shown in Fig. 2 can be the rate-determining step. In simple electrochemical reaction these are in particular mass transport, electron transfer, or surface reactions (adsorption, desorption, crystallization). In more complex reactions, chemical reactions often occur before or after the electrochemical reaction, which can also affect the rate. Therefore, the rate of the sub steps determines the intensity of the current at an applied potential. Above the limiting current density only the mass transport determines the reaction rate. If the current is set above the limiting current density, side reactions occur since the electrons fed to or discharged from the electrodes must undergo a reaction (according to

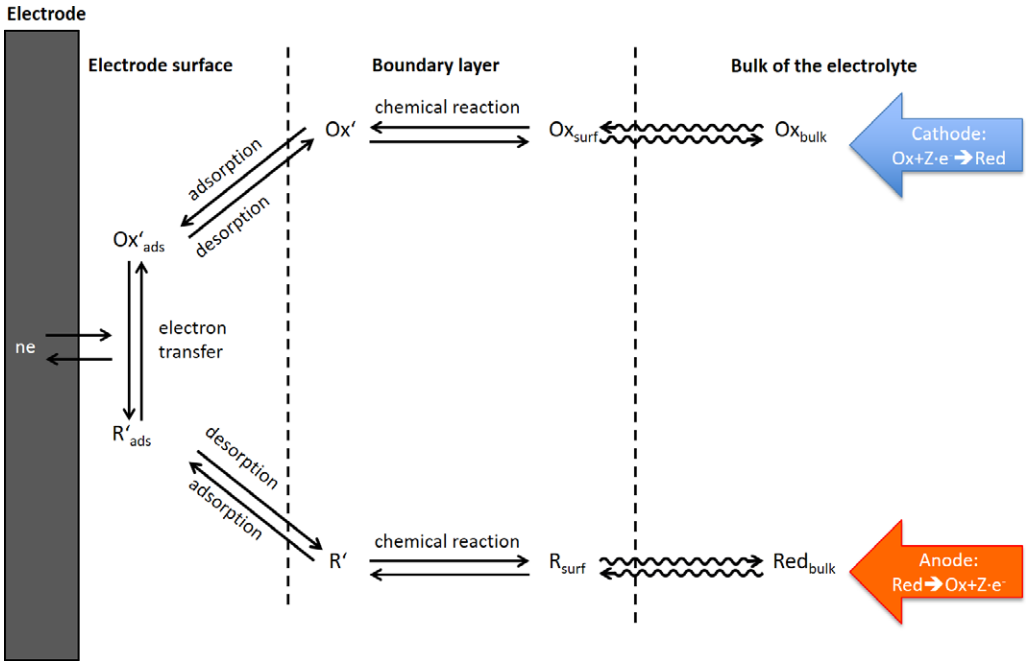

Figure 2. Possible sub steps of electrochemical reactions.

Faraday's law). In most cases, water electrolysis (anodic formation of oxygen and cathodic formation of hydrogen) occur. This side reaction can also be used and adjusted, e.g., to create bubbles in electroflotation for particle separation.

3 Electrical Interconnection, Reactor Design, and Mode of Operation

Electrochemical reactors are used as monopolar or bipolar designs (Fig. 3). This is also applicable to electrochemical reactors for water treatment. In case of monopolar design, the anode and cathode of a cell are immersed in the electrolyte; in the bipolar design, the reverse side of each electrode is the front side of the next electrode. The bipolar design leads to a serial connection of the cells within the reactor, whereas in the monopolar design individual cells are built with an anode and cathode each, which can then be electrically connected in parallel or serially outside the actual reactor via cables. A special design of a bipolar construction is the capillary gap reactor, in which current flows from one electrode to the next through the capillary gaps filled with electrolyte, whereby all electrodes are located in the same, undivided electrolyte chamber (Fig. 4). Versions with porous electrodes are also known [48].

Many electrode geometries and arrangements are generally possible: parallel conductive plane plates, discs, expanded metals or in the form of tube/cylinder as well as spheres or 3D structured bodies. Disc shaped electrodes can also be rotated to improve mass transfer (enhanced limiting current density). Circular electrodes embedded in insulation material are often used for kinetic measurements in the laboratory, disc-shaped electrodes preferably in technical applications. It is also possible to use trickle bed electrodes or fluidized particles.

Another important characteristic is the electrode material or electrode material combination. By selecting the electrode material, the selectivity of the electrochemical reactions can be influenced by utilizing material-specific overvoltages.

The choice of the reactor design, electrode geometries and electrode materials for a specific reactor for water treatment depends largely on the composition and quantity of the water to be treated as well as the objective of the treatment process. To give an impression, examples of electrochemical water treatment reactors are briefly presented. Due to the variety of realized examples of different design, only a selection of reactors of some important processes are given and summarized in Fig. 5.

Like all other chemical reactors, it is also possible to operate the reactor in different modes. The most important operating modes are batch reactor, continuously stirred tank reactor, tube reactor, or a cascade of stirred tank reactors (Fig. 6).

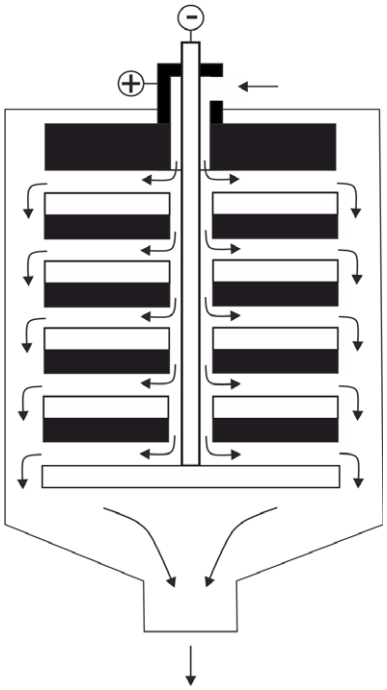

Figure 4. Bipolar electrode assembly in capillary gap reactor [1].

4 Process Description of Established Processes and Future Prospects

4.1 Electrocoagulation

The electrocoagulation process dissolves metal atoms of the electrode materials as ions by charge transfer at the anode [27]. The electrodes are consumed and have to be replaced regularly. In case of packed bed electrode fillings, systems are also known that ensure automatic refilling of the electrodes [49]. Most common materials are iron and aluminum. However, inert materials are also used for (counter) electrodes [28].

Hydroxides are formed through the metal ions in solution and the OH^- ions formed at the cathode enable coagulation or precipitation as well as flocculation of dissolved or colloidal water constituents (e.g., humic substances, dyes) (Fig. 7). During electrocoagulation, water electrolysis at the cathode also

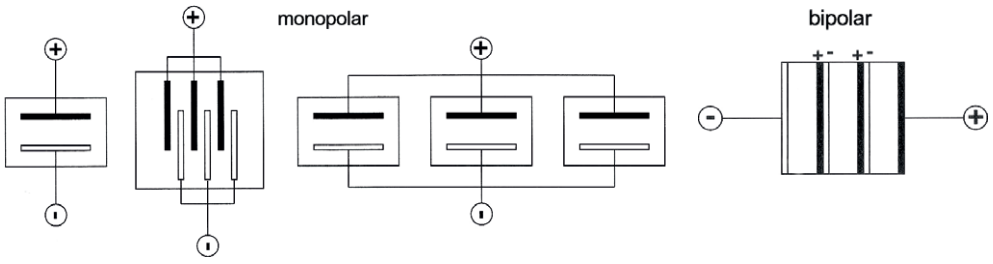

Figure 3. Monopolar and bipolar reactor combinations.

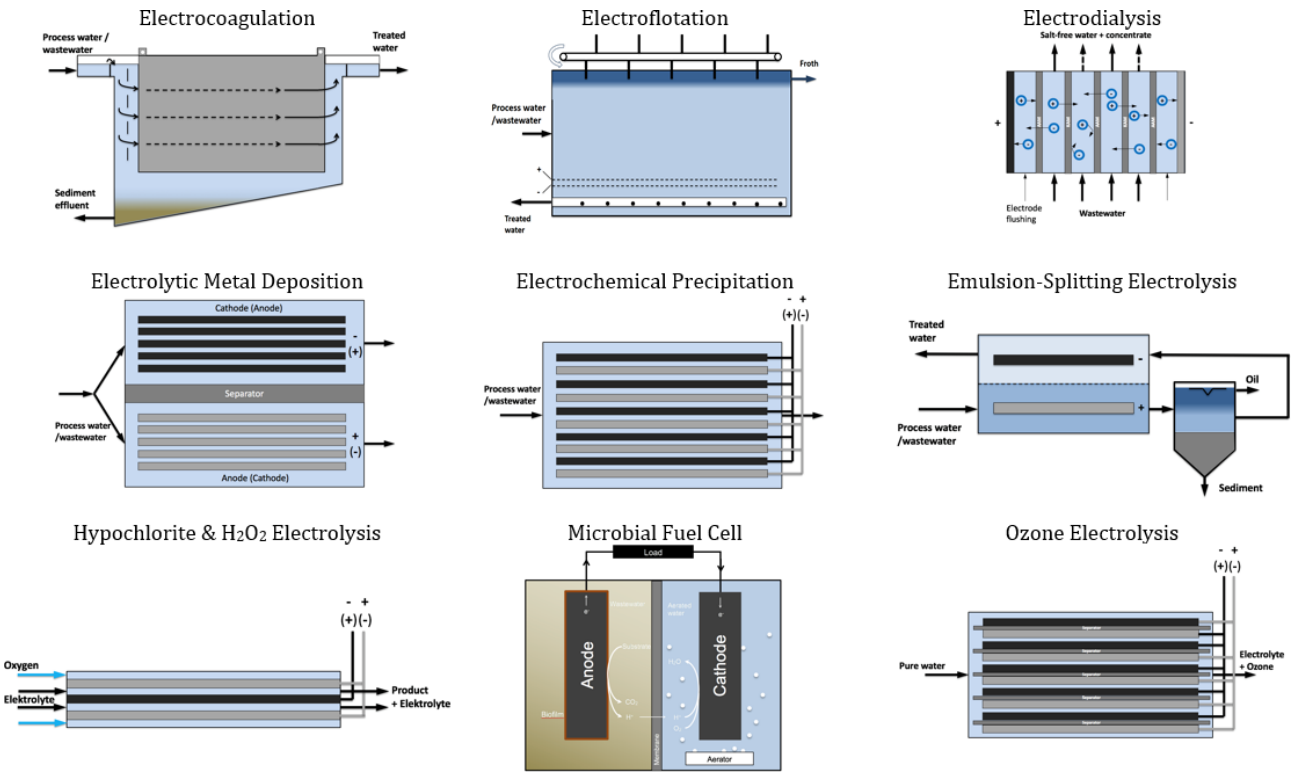

Figure 5. Examples for reactors of some important electrochemical processes for the treatment of different wastewaters.

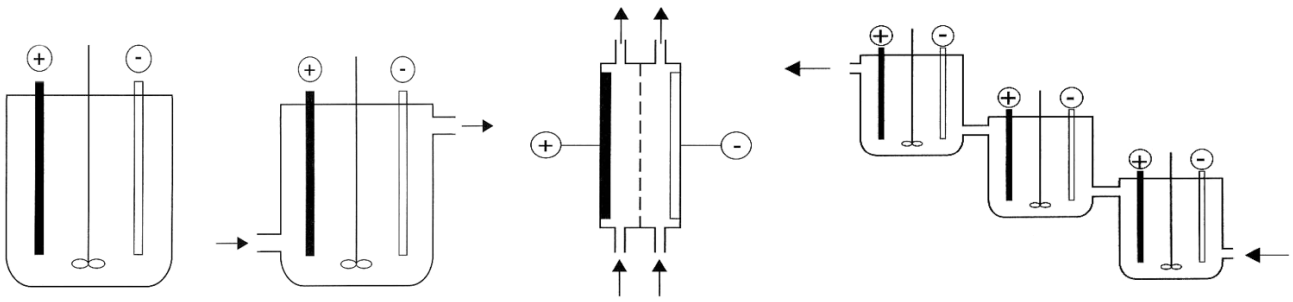

Figure 6. Operating modes of electrochemical reactors for water treatment: batch operation, continuous stirring tank, tube reactor, stirring tank cascade.

generates hydrogen in form of microbubbles. This bubble formation is unavoidable with the mentioned materials and is therefore often used for flotation (electroflotation, see below) and separation of the formed aggregates simultaneously. Therefore, electroflotation is often combined with electrocoagulation (see Fig. 6). In general, microbubble formation is minimized to such an extent that safe plant operation is ensured in conjunction with established safety precautions for monitoring the hydrogen concentration. Depending on the application, the amount of bubbles may be insufficient for an economic flotation effect. As result, a combination of electrocoagulation/electroflotation can also be subject to process limitations for safety reasons. For this purpose, electrocoagulation is often combined with separate solid/liquid separation processes such as sedimentation, filtration, flotation, or pure electroflotation.

The release of OH^- ions leads to an increasing pH value in the bulk solution. The rising pH value is used, e.g., in conjunction with iron electrodes for precipitation of zinc, chromium, and aluminum as the solubility product of Fe(II) hydroxide decreases with rising pH and is thus exceeded. During the formation of hydroxide aggregates, particles, emulsified oil droplets as well as heavy metal ions are also incorporated, deposited, destabilized, and flocculated. Electrocoagulation is also suitable for the removal of sulfides, phosphates, carbonates, dyes, AOX (adsorbable halogenides on activated carbon).

The most characteristic effect of chemical precipitation/flocculation is the rapid pH shift due to the addition of flocculants such as aluminum sulfate and iron chloride. In contrast, the electrochemically induced pH increasement in the process water is significantly slower and for electrochemical

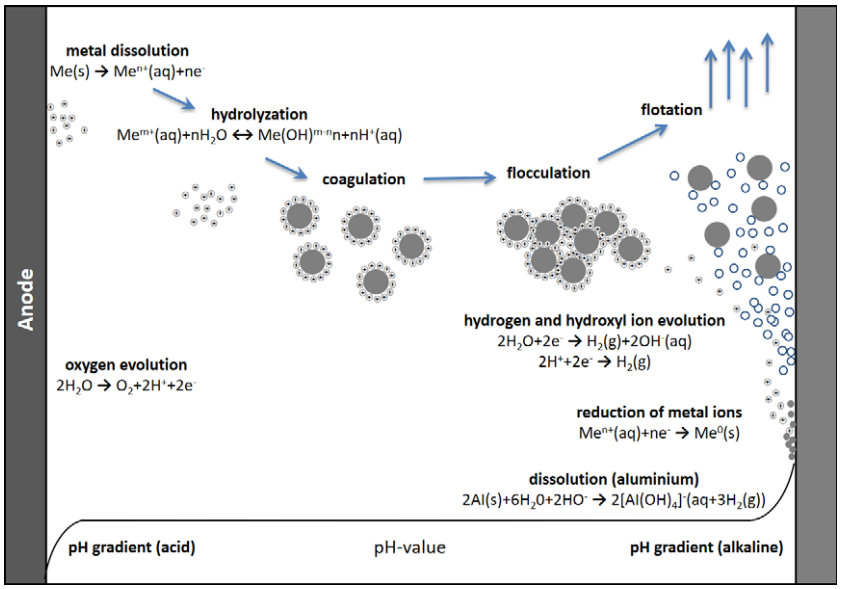

Figure 7. Chemical reactions and processes during electrocoagulation and electroflotation.

applications a sufficiently long treatment time is therefore required. Electrochemical applications would be larger in terms of volume and therefore more suitable for small to medium wastewater volumes [2].

4.2 Electroflotation

Electroflotation is a separation process in which existing hydrophobic particles in water or particles generated by other processes (e.g., electrocoagulation) are carried to the aqueous surface by adhering gas bubbles. This corresponds to the process of a classical foam flotation or dissolved air flotation which is often used, e.g., in the treatment of ores or in wastewater technology. The difference to classical foam flotation is that in electroflotation the gas bubbles are produced by decomposition of water into oxygen and hydrogen. It is also possible to combine electroflotation with electrocoagulation (see above) if one of the electrodes is dissolved by electric current during electrolysis. The released metal ions cause a coagulation of colloidal molecules, which adhere to the gas bubbles formed by the water electrolysis. In electroflotation, the solids can be separated both by the oxygen bubbles and by the hydrogen bubbles. This can take place with different efficiency, depending on the affinity of the gases to the solid. Electroflotation is one of the most effective and versatile methods of electrochemical water purification, as micro gas bubbles are produced and the size distribution of the gas bubbles are very narrow [31].

The choice of current density is crucial for a successful operation. The current density affects the bubble formation rate and diameter together with the resulting mixing intensity in the reactor. In general, a high current density promotes bubble formation and the resulting buoyancy and thus the liquid-solid separation process. Expanded metals, plates or prismatic geometries are used as electrodes, whereby materials are mainly copper, stainless steel, and graphite. Expanded metal-shaped electrodes are often installed horizontally near the bottom of the reactor, while plate-shaped electrodes are installed vertically. Apart from the current density, the bubble size can also be influenced by the electrode wire thickness and the surface quality (roughness). From a fluid dynamic point of view, the systems can be operated in direct current, counter current, or with mixed flow control.

Not all particles of the water load are transported to the surface by the gas bubbles, as the interactions between gas bubbles and solids can be very different. For this reason, a sedimentation zone with bottom outlet for accumulated solids is always provided at the reactors. This process has been well known for more than 100 years and is industrially applied since the 1960s [2, 29, 30].

4.3 Electrodialysis

Electrodialysis enables the concentration or depletion of electrically charged ions and molecules and is a special case of electrochemical reactors. In contrast to the other processes mentioned, in which reaction species are usually produced electrochemically and/or (waste)water constituents are reacted, electrodialysis primarily uses an electrochemical potential as a driving force (migration) for ion-selective membrane processes without a chemical reaction with (waste)water constituents. The type and arrangement of the membranes (ion exchange membranes) and less the arrangement of the electrodes determine the water treatment process. Therefore, electrodialysis is usually categorized as a membrane technology process [16]. Another difference to the other electrochemical processes is that the electrode chambers are spatially separated from the water to be treated. The electrode chambers are usually supplied with auxiliary electrolytes from separate reservoirs in order to remove electrode gases and other reaction products.

Nevertheless, the target setting of electrodialysis has a significant influence on the choice of electrode materials and electrolytes. Depending on the desired ion transport and target product in the reactor chamber adjacent to the electrode, the auxiliary electrolytes must be selected appropriate, e.g., sodium ions or protons in the form of a sodium chloride solution or an acid.

The field of application of electrodialysis is very diverse and allows an extraordinarily large number of possible combinations due to the electrochemically induced ion/molecule migration, the choice of ion supply (e.g., H^+ and OH^-), and the selected membrane type. Electrodialysis processes are used for water treatment (drinking water, process water) of brackish and ground water, complete desalination of water, treatment of rinsing water from electroplating, selective recovery, or concentration of valuable substances from process or rinsing water

(e.g., EDTA, inorganic acids and alkalis, lactic acid, pickling solutions) [16].

4.4 Electrolytic Metal Deposition

In the process of electrolytic metal deposition, the metal ions are electrochemically reduced and, in contrast to electrocoagulation, removed as metals of valence 0. The metal recovered from the (waste)water load can be of high purity and thus a valuable material extraction is possible. The process is not only used for metal separation from wastewater, but also for large-scale production of metals such as copper and zinc. The main field of application in wastewater is the treatment of highly concentrated wastewater. Low concentrated wastewater may firstly be concentrated, because the energy demand of the electrolytic metal separation increases strongly with low conductivity of the treated water, due to the reduced current yield associated with a falling metal ion concentration of the water. Reactors with moving electrodes may compensate this undesirable effect [31]. In the process, the positively charged metal ions move in the electric field between the electrodes to the negatively polarized cathode, where they are reduced to an element and deposited on the electrode surface according to the following equation:

$$Me^{z+} + z\,e^- \rightarrow Me^0 \quad (5)$$

This process is also known as electroplating on an electrically conductive surface, galvanic deposition, or galvano technique [50].

The separation process depends on many factors. For example, metals with higher potential in the galvanic series are more noble and, consequently, first deposited. Furthermore, the process depends on the activity of the metal ion in the solution as well as on the temperature and pH value [51]. In addition to the desired metal deposition, hydrogen formation can occur as a competitive reaction at the cathode. As a consequence, the pH value may have to be adjusted in order to separate the desired ion [52]. The current density is a critical parameter with regard to the deposition quantity per time and the morphology of the deposited metal [53].

4.5 Electrochemical Precipitation

Electrochemical precipitation differs from electrocoagulation due to (1) inert electrode materials, (2) all reactants are already contained in the water, and (3) the pH gradient in the vicinity of the electrodes is used specifically for precipitation, so no or only a sufficient pH shift in the process/wastewater occurs. The objective of this approach is to use the OH^- ions produced at the cathode to precipitate solids. Such a system can also be used to protect other electrochemical reactors and components from scaling [54].

For targeted electrochemical precipitation a material composition is necessary that avoids or minimizes adhesion of the precipitated substances to the electrode surface. Oscillating electrodes promote precipitation in the boundary layer to protect the electrodes. Flexible electrodes made of a material mixture of graphite and electrically conductive polymers are electromagnetically oscillated to precipitate carbonates, phosphates, but also micropollutants such as diclofenac [55].

4.6 Emulsion Splitting Electrolysis

This process is similar to electroflotation, but always requires a combination with a classical liquid-liquid separation operation. In this process, an oil-water mixture that is difficult to separate due to the presence of surface-active substances (e.g., from a car wash) is treated by electrolysis. The charged micelles of the oil droplets are transported to the electrode and discharged on contact. As result, the stabilizer of the oil droplets is missing, the droplets coagulate and rise in the liquid. The oil phase can be separated from the water phase at the top of the reactor. The addition of flocculants is not necessary. The reactor designs can imply plate geometry or a rotationally symmetrical tube shape and the electrodes are often made of iron. An anodic dissolution of the iron can also be desired to promote agglomeration of the contaminants of the water to be treated [2].

4.7 Electrochemical Oxidation (and Reduction)

Electrochemical oxidation processes aim at the mineralization of organic compounds in process waters and wastewaters [25], whereby in particular the electrochemical advanced oxidation processes (E-AOP) have moved into focus of research and application. These are characterized by the generation of very strong oxidizing agents such as hydroxyl radicals, preferably using the reaction at the anode. The in situ electrochemically generated oxidants occur either directly at the anode surface [56] or indirectly by subsequent reactions with inorganic components [5].

For direct oxidant generation, electrodes are mostly used which generate hydroxyl radicals through the oxidation of water (Fig. 8, anode side, dashed line). This species has a very high standard potential (2.8 V vs. SHE) whose oxidation power is only exceeded by active fluorine [57]. Although unspecific reactions are the result due to the high potential, a manifold reaction network [58] is possible, also to other oxidizing agents [37].

Reactive oxygen species also contribute to organic degradation, which can arise from the reaction network of hydroxyl radicals and molecular oxygen (Fig. 8, anode side, chain line) [59]. In addition, the formation of active chlorine species (Cl_2, HOCl, OCl^-) [60–65], hydrogen peroxide [66] and/or ozone [67, 68] is possible (Fig. 8, anode side, light grey and black lines) as well as the formation of superoxides (O_2^-), e.g., in the form of peroxodisulfate and peroxycarbonate [23, 69]. However, the nature of electrochemical mineralization is even more diverse. In the mediated electrochemical oxidation, stable compounds such as metal ions are first oxidized to highly reactive species, which then oxidize the impurities and/or form hydroxyl radicals [35]. Depending on the wastewater matrix to be treated and the process parameters (current densities, flow conditions, etc.), the direct oxidation of the organic compounds

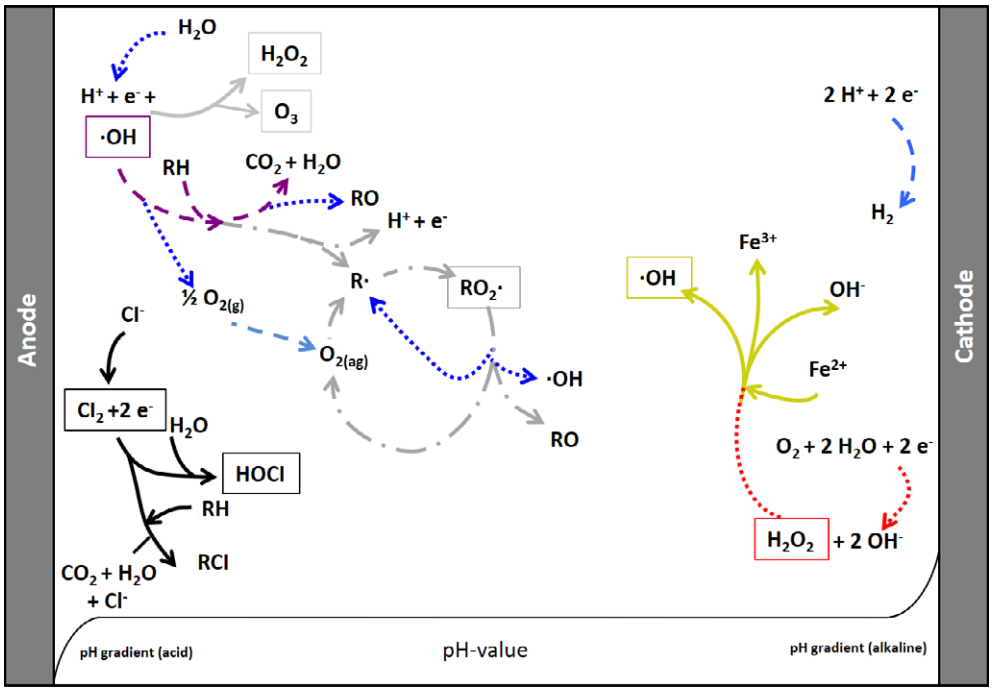

Figure 8. Reaction paths of electrochemical oxidant generation for electrochemical treatment of organic compounds and disinfection. Electrogenerated H_2O_2 and O_3 (anode side, light grey line); oxidation of organic compounds by hydroxyl radicals (anode side, dashed line); oxidation with oxygen radicals (anode side, chain line); halogenation (black line); cathodic hydrogen formation (dashed line); cathodic peroxide formation (dotted line); Fenton activation (cathode side, bold line).

at the anode surface also takes place [70]. Some compounds can be degraded more easily by the combination of oxidation and reduction than by pure oxidation and an undivided electrochemical system or sequential process control is chosen for the alternating degradation mechanism [71]. An often studied and commercially available E-AOP systems on a small scale are based on boron-doped diamond electrodes (BDD) [23, 72] on the anode and cathode sides, whereby other anode materials are also possible (Tab. 2).

The advantage of the BDD/BDD combination is the possibility of electrode polarity reversal. This enables to dissolve products adhering to the electrodes in course of undesired precipitation caused by high (cathode) or low (anode) pH values at the electrode surface (and boundary layer) [76]. The disadvantage of this electrode combination is that the electrode switched as cathode does not achieve any purification performance since mainly hydrogen (Fig. 8, dashed line) and hydroxide ions are produced (as well as a direct reduction at the cathode, depending on the compound). Therefore, recent investigations aim at the combination with hydrogen peroxide-forming cathodes to generate oxidizing agents at both electrodes simultaneously. This leads to a higher and more energy-efficient degradation of organic compounds [77]. Hydrogen peroxide can also be activated to hydroxyl radicals, e.g., by Fenton's reaction (Fig. 4, cathode side, full line) [78]. Electrochemical oxidation is also coupled with other processes, e.g., in combination with electrocoagulation [74], electrosorption [79], or ozonation (generated by a high-voltage or UV/ozone generator) [80].

The advantages of electrochemical oxidation processes are the high purification performance, especially in operation with BDD electrodes, and that the system requires no additional chemicals. On the other hand, the disadvantages comprise the high investment and operating costs [5] as well as the formation of undesirable by-products such as perchlorate [81]. Especially in the presence of halides, the halogenation of the organic compounds takes place, whereby these by-products could be significantly more toxic than the starting material [82]. One possibility to avoid the by-products is the complete electrochemical oxidation of the organic compounds to carbon dioxide and water, which requires longer treatment times. Further possibilities exist in combination with other processes, e.g., within the scope of multi-barrier concepts, the treatment of concentrated water/wastewater partial streams, or useage of very high pH values within the E-AOP [83].

4.8 Electro-Fenton

In the classical Fenton process (named after Henry John Horstman Fenton; end of the 19th century) hydrogen peroxide reacts with iron ions to form highly reactive OH radicals, which in turn react with dissolved organics, germs, bacteria, and colloids up to complete mineralization. The individual reaction steps of the Fenton process are:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (6)$$

$$RH + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O \quad (7)$$

$$R + Fe^{3+} \rightarrow R^+ + Fe^{2+} \quad (8)$$

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \quad (9)$$

The organics are removed in a two-step process: oxidation and coagulation. Oxidation is given by the reaction of OH radicals with the organic compounds in water while coagulation takes place at the same time by an iron complex. The Fenton process works best at a pH value of 3 [84].

Table 2. Anode materials for E-AOP systems.

Anode material	Advantages	Disadvantages	Comparison to other electrodes	Ref.
Ti	Stable	Passive, expensive		[5]
Pt	High chemical stability, low overvoltage for oxygen evolution, high proportion of direct oxidation	Expensive	Low efficiency in anodic oxidation of organic compounds	[5]
PbO_2	Cost-effective, high current yield, efficient in EO, high overvoltage for oxygen evolution, simple production	Susceptible to corrosion, hazardous to health and the environment due to dissolved Pb^{2+}-ions		[5, 46]
SnO_2	Increased current yield of ozone, mostly chemically and electrochemically inert		Lower degradation rates compared to BDD	[73]
D S A (Dimensionally Stable Anode)	Enable indirect oxidation, high current yield, increased overvoltage for oxygen evolution, commercially available. Depending on the type, ozone generation is also possible (e.g., Ta_2O_5-IrO_2; Nb_2O_5-IrO_2), reasonably priced	Not long-term stable, insufficient electrochemical stability		[5, 74]
B D D (Boron-Doped Diamond electrode)	Largest potential window in an aqueous electrolyte, very high chemical and electrochemical stability, high overvoltage for oxygen evolution, high current yield of hydroxyl radicals, corrosion-resistant, good conductivity	Very expensive	Increased activity	[5, 23, 36, 75]

The advantage of the electro-Fenton process is that at least one chemical for the Fenton process is produced in situ in an electrochemical reactor. The following possibilities are conceivable [85]:

- Production of H_2O_2 at the cathode, production of oxygen at the anode, external addition of Fe^{2+}
- Generation of H_2 at the cathode, generation of a Fe^{2+} solution at a sacrificial anode, external addition of H_2O_2
- Generation of H_2O_2 at cathode, generation of Fe^{2+} solution at sacrificial anode

In the third case, no additional dosage of chemicals is required, making the process easy to perform. The in-situ formation of reactive hydrogen peroxide avoids the problem of storage and handling. The disadvantage of this process is the formation of a ferrous sludge which has to be disposed. Recent processes work with membranes; thus, it is possible to avoid the discharge of the iron hydroxide sludge [41].

4.9 Microbial Fuel Cell

The microbial fuel cell (MFC) uses the chemically bound energy of organic load in wastewater for a direct conversion into electric current, simultaneously purifying the water [86]. The direct conversion of chemical energy into electrical energy is made possible by the use of electroactive bacteria, which grow on the surface of the anode as a dense biofilm. The anode is immersed in wastewater, which must be oxygen-free. Different wastewater types can be used as substrate sources, e.g., brewery wastewater [87], dairy wastewater [88], or municipal wastewater [86]. In the latter case, electroactive bacteria are already present and a targeted inoculation of the anodes is therefore not necessary.

The bacteria absorb the energy by metabolizing the organic load of the wastewater in form of colloids, but mainly in the form of dissolved organic substances [86]. Trace substances such as sulfamethoxazole [89] as well as germs [90] can also be eliminated in an MFC system by targeted cultivation. Note that elimination does not mean degradation since transformation products may be formed which may not be degraded further.

During the metabolic process, electrons are released by bacteria into the environment. In case of the MFC, the electrons are released to the anode, whereby those electrons can be transferred via three mechanisms: directly, via mediators, or via nanowires [91].

To balance charges in the electrolyte, ions migrate from one electrode chamber to another. These can be, e.g., H^+ ions that are formed at the anode. In order to close a current circuit and finally drive a load, a coupled counter-reaction at the cathode is required. On laboratory scale, potassium hexacyanidoferrate(III) is often used as the final electron acceptor. During the reaction, the trivalent prussian red is reduced to the divalent

yellow colored salt. Although relatively high power densities are achieved with this type of cathode in experimental plants [92], this is not relevant in practice since potassium hexacyanidoferrate(III) must be permanently added and the salt is toxic. For practical applications, oxygen is more suitable as final electron acceptor, since oxygen is available in sufficient quantities in the air and is not toxic.

Since the cathode is often the limiting electrode in an MFC, new, inexpensive, and non-toxic catalysts for oxygen reduction are under development. So far, different graphites, platinum, and manganese dioxide have been investigated [93, 94].

The low voltages and current densities of the MFC result in very low power densities of approx. 1 W m^{-2} [95] compared to classical and purely chemical fuel cells, for which reason no commercial success of the microbial fuel cell has yet been reached.

4.10 Hypochlorite Electrolysis

In drinking water treatment, various methods are used to disinfect water (see Drinking Water Ordinance), whereby the amount of added chemicals, the by-products, and the depot effect greatly vary. Sodium hypochlorite (NaClO/HClO) provides a good depot effect with a high purification effect due to low doses (max. 1.2 mg L^{-1} free chlorine) [42]. In the aqueous state, the weak acid HClO is not stable and decomposes under light and/or heat [96]. The electrochemical generation of HClO offers the advantage of in situ and demand-oriented generation in the required concentrations, which only requires the provision of a sodium chloride solution (and possibly oxygen – see below).

Various electrolysis processes are known for the production. For example, conventional chlor-alkali electrolysis can be used (Fig. 9, (1)), whereby in a subsequent process step the formed chlorine is introduced into a sodium hydroxide solution [19].

If the hazard potential due to the gases formed (avoidance of detonating gas through hydrogen and chlorine) can be reduced by skillful operation, an operation without a membrane is also possible (Fig. 9, (2)) and NaOCl formation takes place directly in the undivided reactor [97, 98]. The most elegant but in literature least considered electrolysis cell for the production of hypochlorite comprises a chlorine-forming anode and an oxygen-reducing cathode. This configuration avoids the formation of hydrogen (Fig. 9, (3)), drastically increases the operational reliability with a separator-free operation, and the hypochloride is formed directly in the electrolysis cell. In addition to the use of hydroxide ion-forming cathodes, the use of hydrogen peroxide-forming cathodes is also suitable to increase the cleaning effect of the system (dashed reaction path in Fig. 9) [99]. Due to the wide variety of chlorine species (especially chlorine, hypochlorite, chlorate, perchlorate) and the associated equilibrium reactions, reaction control is complex and requires defined temperature and pH values [100]. Such systems are not only suitable for drinking water disinfection, but also wherever a disinfecting depot effect is required.

4.11 Hydrogen Peroxide Electrolysis

Hydrogen peroxide can be produced electrochemically by cathodic reduction from oxygen or atmospheric oxygen (Fig. 8, cathode side, dotted line). Especially due to the use of gas diffusion electrodes (GDE), the conversion of oxygen is no longer

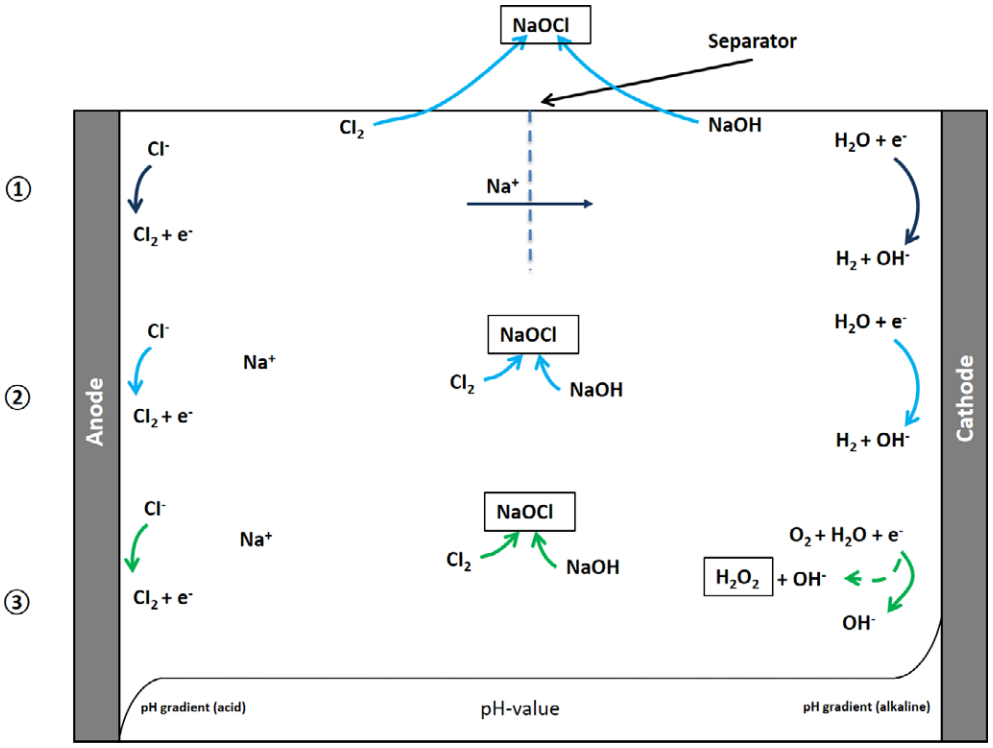

Figure 9. Reaction paths of possible reactor concepts for hypochlorite production.

limited by the amount of oxygen dissolved in the electrolyte. While the electrolyte is in contact with the electrode on the front side of the GDE, it is supplied with oxygen/air on the backside (over stoichiometric) [31]. Even if such a process would have many benefits, e.g., for the disinfection of surfaces, no commercial system is yet available. This is mainly caused by the GDEs, which can only be operated at low current densities and are commercially available only in laboratory scale. In addition, the generation of hydrogen peroxide is only possible electrochemically in combination with hydroxide ions (or proton consumption) [31, 78]. For this reason, catalysts and electrode composition in general are currently subject of research [101, 102].

4.12 Ozone Electrolysis

The treatment of wastewater by ozonation is state of the art. For this purpose, an ozone generator is commonly used, which generates ozone from oxygen or air through silent electrical discharge or UV light. Subsequently, the generated ozone is transferred into the wastewater by a gas and liquid contact apparatus. In electrochemical reactors, ozone is generated directly in the water [80, 103, 104]. While the generation of ozone is also used in situ in E-AOP water treatment (see Sect. 4.3), such electrolysis cells also offer the possibility of an on-demand, electrochemical production of ozone for direct use [105]. In addition, these can also be cheaper for certain applications than conventional methods.

In the past, numerous electrode materials have been investigated for this purpose, but the commissioning of technically relevant pilot plants are based on boron-doped diamond electrodes.

For the electrochemical operation of diamond electrodes, the choice of process parameters has a strong influence on the yield. Especially electrolytes with very low conductivity as well as high volume flows are decisive for a high ozone yield and concentration [106]. In order to keep the voltage losses low despite the very low electrolyte conductivities, the anode and cathode are placed directly on a membrane ("zero gap" arrangement) [105].

5 Conclusion and Outlook

Against the background of the increasing global demand for water, the requirements for water treatment will increase considerably in the future. Climate change and the expansion of arid and semi-arid regions will also contribute to this. In order to decouple industrial growth from water supply, energy- and raw material-efficient water recycling is necessary. It is proposed that electrochemical processes will be able to make a major contribution to this challenge, because these techniques can be used in a wide variety of ways – as selective separation technology and/or degrading processes, enabling chemical-free wastewater treatment. Furthermore, electrochemical processes have recently undergone a considerable increase in new developments.

The design and interconnection of electrochemical reactors are diverse and depend on the application objective as well as on the material properties and shape of the electrodes. This article therefore summarizes established and future-oriented electrochemical techniques for water treatment with respect to the background of the treatment objectives and provides a systematic overview of specific reactors and configuration possibilities.

Certainly, there are still some challenges for further developments and sustainable all-in-one solutions in this area. These include electrode costs for radical oxidation, passivation or fast material destruction of electrode surfaces due to deposits or energy requirements. New approaches to this are shown in the article, such as the multiple use of the current for additional oxidation species generation or the concept of electrochemically pH-induced precipitation or the in situ production of hydrogen peroxide to avoid the transportation of this reactive reagent.

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Thorben Muddemann, born in 1988, completed his studies in Process Engineering at Clausthal University of Technology in 2015 with a M.Sc. thesis on electrochemical wastewater treatment. During his studies, he worked for Covestro AG and has been interested in electrochemical processes ever since. Since 2016, he has been employed at the Institute of Chemical and Electrochemical Process Engineering at Clausthal University of Technology, where he is working extensively on electrochemical wastewater treatment, in particular electrolysis and microbial fuel cells.

Dennis Haupt, born in 1987, completed his studies in Environmental Protection Technology at Clausthal University of Technology in 2016 with his diploma thesis on "Microbial Fuel Cells". Since then, he has been working at the CUTEC Research Centre at Clausthal University of Technology in the Department of Wastewater Process Engineering. He continues to work on microbial fuel cells, the electrochemical treatment of wastewater as well as other issues in wastewater treatment.

Michael Sievers, born in 1963, began his studies in Mechanical Engineering/Process Engineering at Clausthal University of Technology in 1981 and graduated as Dipl.-Ing. in Process Engineering in 1989. He then joined CUTEC-Institut GmbH and received his doctorate from TU Clausthal in 1993. Since 1995, he has been responsible for various research areas as Head of Department. In March 2007, he was appointed honorary professor at the TU Clausthal. Since August 2017, he has been Head of the Department of Wastewater Process Engineering at the CUTEC Research Centre at Clausthal University of Technology.

Ulrich Kunz, born in 1956, studied Chemistry at Clausthal University of Technology. He received his doctorate (1988) and his habilitation (1998) in Chemical Engineering. Since 2003, he has been professor at Clausthal University of Technology and head of working groups at the Institute of Chemical and Electrochemical Process Engineering. His research activities focus on the development of catalysts and microreactors for organic syntheses, the development of coating processes for electrodes, the investigation of reactors for (electro)chemical conversions and the optimization of processes together with industrial partners.

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